

E. M. F., RESISTANCE AND CAPACITANCE PHENOMENA
IN PHOTOVOLTAIC CELLS CONTAINING
GRIGNARD REAGENTS

BY
HARRY EMMONS HAMMOND, M.S.

The Abstract of a Thesis Submitted in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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UNIVERSITY OF MISSOURI

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ABSTRACT

E.m.f., resistance, and polarization capacitance have been measured in light-sensitive cells containing ether solutions of Grignard reagents in an effort to determine whether the known voltage variations with illumination are due to ionization changes or to electrode-film variations. Voltage alterations with illumination or x-ray irradiation are described. Resistance variations with illumination are found in ethylmagnesium bromide cells but not in phenylmagnesium bromide cells until a "forming" process has been carried out. Solvation changes seem to offer a more reasonable explanation than ionization changes. Capacitance changes seem unrelated to resistance or voltage changes. Unsymmetrical resistances are noted in several cases. Capacitances as high as 7 mf per cm² of electrode area have been found. Film thicknesses are estimated to be of approximately molecular dimensions, greater for benzene-ring compounds than for short-chain compounds. Voltage variations are thought to be due to phenomena taking place on or very near electrode surfaces.

THE Becquerel effect is the name applied to an alteration of the electromotive force of a voltaic cell upon exposure of the cell to light. Originally found by Becquerel¹ to take place in a cell having platinum or silver plates coated with a silver halide and immersed in dilute sulphuric acid, the effect was later discovered by Rigollot² to exist with solutions of fluorescent dyes. Now the effect is known to be very common. Through the work of Nichols and Merritt,³ Hodge,⁴ and others, the effect has been shown to be located at or very near the electrode surface in the case of the dye solutions. Goldmann⁵ offered a theory based on the photoelectric effect. Baur⁶ proposed a photochemical theory for the effect, which has been upheld by Garrison,⁷ Tucker,⁸ and Russell⁹ among others. A reasonably comprehensive survey of the work carried on with solutions in water and in absolute alcohol is presented by Lifschitz and Hooghoudt.¹⁰

¹ E. Becquerel, *Compt. Rend.* **9**, 145 (1839).

² M. H. Rigollot, *Compt. Rend.* **116**, 878 (1893).

³ Nichols and Merritt, *Phys. Rev.* **19**, 415 (1904).

⁴ P. Hodge, *Phys. Rev.* **28**, 25 (1909).

⁵ A. Goldmann, *Ann. d. Physik* **27**, 449 (1908).

⁶ E. Baur, *Zeits. f. Phys. Chemie* **63**, 683 (1908).

⁷ A. D. Garrison, *Jour. Phys. Chem.* **28**, 334 (1924).

⁸ C. W. Tucker, *Jour. Phys. Chem.* **31**, 1357 (1927).

⁹ H. W. Russell, *Phys. Rev.* **32**, 667 (1928).

¹⁰ Lifschitz and Hooghoudt, *Zeits. f. Phys. Chemie* **128**, 87 (1927).



A number of papers have been published on the luminescence of Grignard compounds, organo-magnesium halides, under suitable conditions.^{11,12} Kondyrew¹³ showed that cells containing ether solutions of ethylmagnesium bromide produced an e.m.f. He also measured the temperature-resistance coefficient. Such cells show the Becquerel effect.^{11,12} Considerable work, much of it as yet unpublished, has been done by others on the variation of the e.m.f. of Grignard cells with changes in illumination, in wave-length of light used, in temperature, etc.

The primary purpose of this investigation was to uncover new evidence as to whether the photovoltaic effect in Grignard cells took place on or near the electrodes or in the body of the electrolyte. A photoelectric effect should produce a change in the conductivity of the solution and an alteration in an electrode film might cause a detectable change in the cell capacitance. The method employed contemplated tests of many such cells, first as to the nature and magnitude of e.m.f. alterations, second as to the existence and magnitude of any resistance and capacitance changes under exposure to light or to x-rays. The results obtained suggested a further investigation of certain of the effects of electrolysis on these cells, a feature not originally planned. Certain interesting results were obtained.

Most of the cells were made up in one-inch test tubes with the electrodes mounted on glass tubes passing through rubber stoppers. The supporting wires were either of the same materials as the electrodes or else the electrodes were long enough to keep the wires out of the solutions. A few H-cells with one electrode in each arm were used. Some cells hermetically sealed in glass were made, since it was desired to test whether the properties were retained for a long time, if the evaporation of the ether was prevented. The Grignard reagents were made in an atmosphere of nitrogen, but in the solution there may be formed an etherate of the magnesium halide. It has not been possible to determine how far these etherates influenced the actions noted. The compounds used were phenylmagnesium bromide, ethylmagnesium bromide, the corresponding iodides, and bromo-ethylmagnesium bromide. These compounds were used because previous work by others had shown that they gave the largest photovoltaic responses. Various concentrations and electrode combinations were used.

The cells were mounted in a constant-temperature water bath packed in sawdust in a large light-proof box provided with a window and sliding shutter. Each cell was in a separate stall. A shielded cable ran from the cell-box to a selector panel by which any cell could be connected to the measuring apparatus. A 1000-watt lamp was used as the light source and the light was concentrated upon the cell under test by means of a large glass lens. An x-ray tube was also available.

¹¹ Dufford, Nightingale, and Gaddum, *Jour. Am. Chem. Soc.* **49**, 1858 (1927).

¹² R. T. Dufford, *Jour. Opt. Soc. Amer.* **18**, 17 (1929) and R. T. Dufford, *Phys. Rev.* **33** 119 (1929).

¹³ N. W. Kondyrew, *Ber. D. Deutsch. Chem. Gesell.* **58**, 464 (1925).

A Leeds and Northrup potentiometer, type 7651, was used for e.m.f. measurements and the slide-wire of the same instrument with extensions for the ratio-arms of the bridge. A microphone hummer and a tuned vacuum-tube oscillator gave 1000-cycle current for the bridge. The oscillators were remote from the bridge and current was brought up by a shielded cable. The bridge circuit was that described by Jones and Josephs¹⁴, but a two-mf mica condenser was connected in series with the cell to prevent the possibility of polarization. Without this precaution, it was found that resistance and e.m.f. changed so rapidly under test conditions that measurements were meaningless. A diagram of the bridge is shown in Fig. 1.

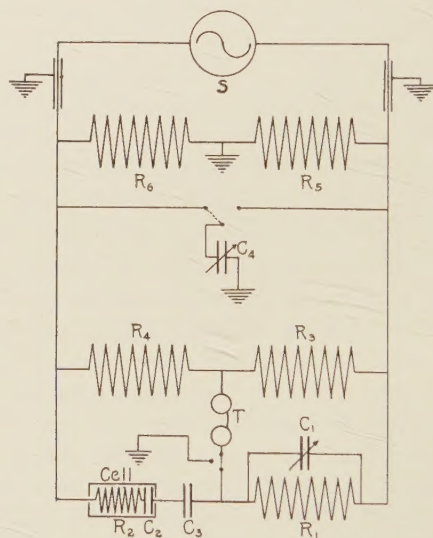


Fig. 1. Diagram of bridge circuit.

The theory of this bridge is the same as that given by Jones and Josephs with the insertion of the capacitance of the condenser mentioned above. In order to balance this bridge, two conditions must be fulfilled, as follows:

$$R_2 = \frac{R_1 R_4}{R_3} \left[\frac{1}{1 + R_1^2 C_1^2 \omega^2} \right] \quad (1)$$

$$C_2 = \frac{C_3 (R_1^2 C_1^2 \omega^2 + 1)}{R_1^2 C_1 \omega^2 (C_3 - C_1) - 1} \quad (2)$$

In these equations R_2 and C_2 are the resistance and capacitance of the cell, the capacitance being treated as in series with the resistance. R_3 and R_4 are the ratio-arms of the bridge, which were kept equal for the most part. C_3 is the capacitance of the condenser connected in series with the cell, and C_1 a variable capacitance in parallel with the known resistance R_1 .

¹⁴ Jones and Josephs, *Jour. Amer. Chem. Soc.* **50**, 1049 (1928).

The other resistances and capacitances are parts of the modified Wagner ground. The parenthetical correction factor in Eq. (1) is usually near enough to unity to be safely neglected, but in some of the cells tested here it was found to be as low as 0.75. Eq. (2) made possible the computation of the cell capacitance from data obtained during the measurement of the cell resistance. It can be seen that the balance conditions are functions of the frequency of the bridge current. Since the oscillators both gave out several harmonics, it was never possible to obtain complete silence in the phones, but merely to balance out the fundamental.

A number of tests were made which indicated that the resistance measured by the bridge was the electrolytic resistance and was very slightly affected, if at all, by films on the electrodes. For example, tests showed that variations of the distance between electrodes produced proportional changes in the resistance.

When an approximate value of the cell-resistance was known, bridge readings could be taken every minute. Potentiometer readings were taken at one-minute or half-minute intervals. Usually cells were illuminated for five minutes and then allowed to remain dark for an equal period.

The tests made can be classified under four general headings, which will be discussed in turn.

(a) *The effects of illumination and mechanical agitation on e.m.f.* Every cell was tested in this way. Ordinarily the entire cell was illuminated. With H-cells, tests were also made by illuminating separate electrodes or the cross-bar. In a few cases, a slit was placed in front of a straight cell so that a narrow ribbon of light passed parallel to the electrode surface or merely through the solution. Tests were made with varying degrees of mechanical agitation. As most of this part of the work was a repetition of what had been done by others, only the general conclusions will be given.

The e.m.f. was greatly affected by agitation of the cell and by polarization. The photovoltaic effects occurred without noticeable temperature changes. Oscillations of e.m.f., due to some unknown cause, took place even in the dark. Any change in the electrode surface caused an e.m.f. change, for example, exposing the electrode to air for a moment, cleaning the surface, etc. E.m.f. changed with age of the cell, partly because of concentration changes and partly no doubt because of slow electrolysis by minute leakage currents. Cells sealed in glass retained properties for many months but the e.m.f. varied and also the magnitude of the photovoltaic response. Light affected the potential of a given electrode almost invariably in the same way. Illumination of the electrolyte alone produced very small effects, possibly due to scattered light reaching the electrodes. In a few cases readings closely spaced showed that the light-e.m.f. effect involved two or three successive alterations. These were shown, by illuminating first one electrode and then the other by means of the narrow slit, to take place part near one electrode and part near the other, but very little, if any, in the body of the liquid. These tests, in general, favored the belief that the voltage phenomena are mainly localized near the electrodes. As a whole, these

conclusions are in agreement with those given in papers by the writer's colleague, R. T. Dufford, already quoted^{11,12} or soon to be published.

(b) *Measurements of e.m.f. as affected by irradiation with x-rays.* The general results obtained upon exposing certain cells to a beam of x-rays have already been reported in a brief note.¹⁵ Although they gave some promise as a means of measuring x-ray intensities, there were uncertainties about their behavior which need clearing up. This x-ray response differed from that produced by visible light in magnitude and frequently in sign, indicating that it was a different sort of action. Fig. 2 is a typical graph.

(c) *Measurements of e.m.f., resistance, and capacitance of cells as affected by visible light or by x-rays.* The accuracy of resistance measurements was about 0.1 percent, while that of the capacitance measurements was about

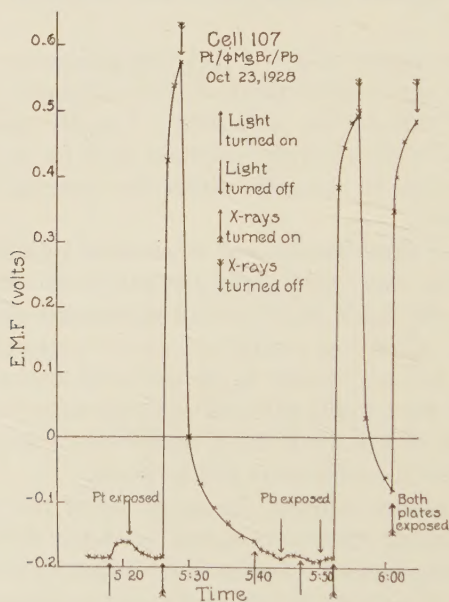


Fig. 2. E.m.f. as affected by light and x-ray illumination.

1 percent. Values of the cell-capacitances found by this bridge agreed with those indicated by a Leeds and Northrup Farad Bridge. All the cells studied carefully were of the test-tube type with electrodes about 5 mm apart. Platinum electrodes were of 1 cm² area, most of the others were of 5 cm² area. Resistance of a cell ranged between 500 and 20,000 ohms, capacitance from 0.4 to 35 mf.

Seven cells contained phenylmagnesium bromide with various electrode combinations. None of these cells showed any change in resistance upon exposure to light when the cells were new, but one, with platinum and copper electrodes, developed such sensitivity after about six months. The light-induced change was a drop of about 1 percent in resistance, recovery taking

¹⁵ R. T. Dufford and H. E. Hammond, Phys. Rev. **33**, 124 (1929).

place in an equal period. Temperature rise produced an increased resistance which persisted as long as the cell was observed, indicating that the light effect was a different phenomenon.

Two cells filled with ethylmagnesium iodide gave no definite light-resistance response.

Four cells contained ethylmagnesium bromide. These were all symmetrical cells with electrodes of aluminum, platinum, copper, and sodium respectively. These cells showed lower resistances than those containing phenylmagnesium bromide. The resistances decreased and the capacitances increased with age in general. A single cell with platinum and aluminum electrodes and containing bromo-ethylmagnesium bromide showed a high

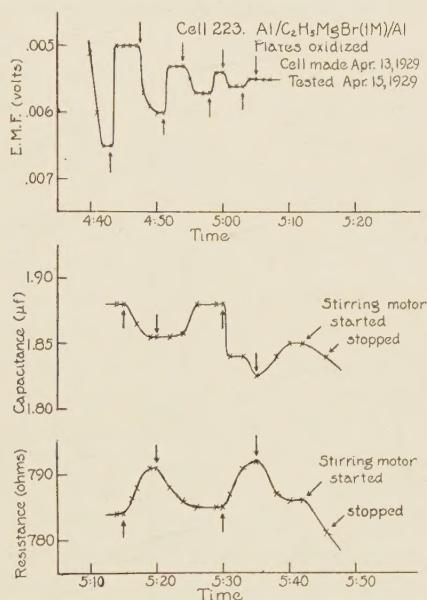
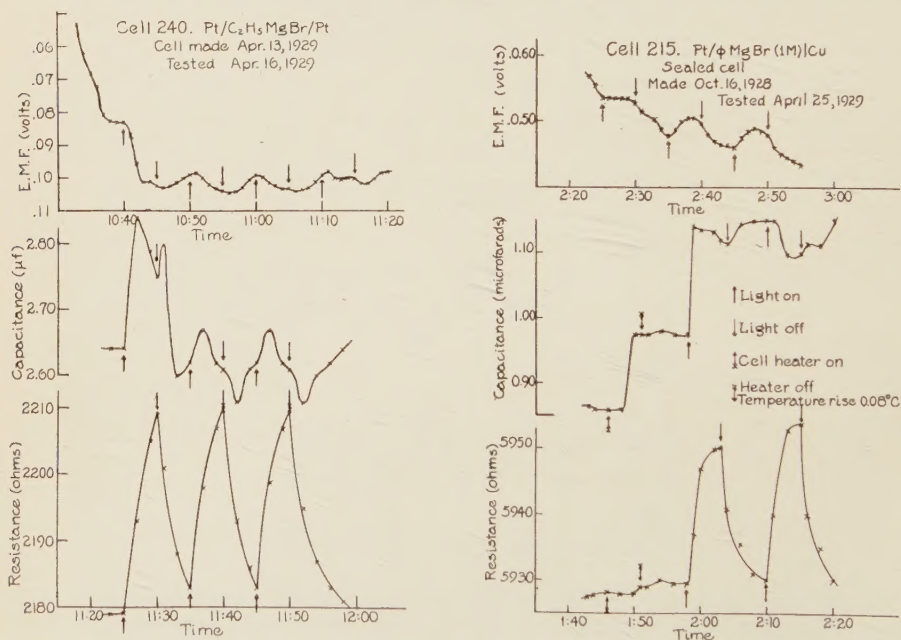


Fig. 3. Effect of light on e.m.f., resistance and capacitance. Upward-pointing arrows indicate when light was turned on; downward-pointing arrows when light was turned off. The same notation is followed in succeeding figures.

initial resistance, which became smaller with age, while the capacitance increased. All these cells showed an increase of about 1 or 2 percent in resistance during five minutes illumination, followed by recovery in an equal period of darkness. The changes in resistance could be detected within a few seconds after turning on or off the light. Resistance changes due to temperature rise could not be detected so soon and the changed value usually persisted after the temperature had come back to the original level. Furthermore, these light-induced changes were not in the same sense as those due to temperature rise in all cases. Figs. 3, 4, and 5 show typical sets of results. It was not possible to trace any general interrelation between the changes in e.m.f., resistance, and capacitance when the cells were illuminated. Fig. 4 shows the only example found of any apparent regular relation between

the capacitance values and the presence or absence of light on the cell. This relation existed for only a part of the test, as can be seen.

No tests of specific resistance were made for the Grignard solutions, but the values must be high in view of the high resistances compared with the cell dimensions. Secular variations in resistance ran as high as 50 or 60 percent, while the light-induced changes never exceeded 2 percent. The former changes were not reversible, the latter were. The photoelectric hypothesis is not tenable as some of the light-induced changes were increases in resistance. Neither does it seem reasonable to attribute a voltage variation of from 10 to 50 percent to a process which caused a resistance change of only 1 or 2 percent. The secular changes in resistance were undoubtedly due to chemical changes in the cell composition, evidences of which sometimes be-



Figs. 4 and 5. Effect of light on e.m.f., resistance, and capacitance.

came evident to the eye as time went on. The writer believes that the light-induced resistance changes were due to temporary and reversible variations in solvation of the ions rather than in percentage of ionization. These data, therefore, served to strengthen the idea that the voltage phenomena are due to changes near the plate surfaces, but the lack of any consistent relation between the capacitance changes and the presence or absence of light did not give any definite evidence to locate the seat of action on the surface itself.

Operation of the x-ray apparatus caused so much noise in the phones that the bridge could not be balanced while the cell was being irradiated. If the resistance or capacitance was affected by x-rays, the effect did not persist long enough to be measured after the apparatus was shut off.

As the high-frequency bridge current sometimes altered the e.m.f. of the cells, the potentiometer tests were always made first and the bridge measurements as soon as possible thereafter.

(d) The development of light-resistance sensitivity in one phenylmagnesium bromide cell after several months suggested that electrolysis of these cells might yield some interesting results. The high values of the capacitance per unit area in several of the cells also increased the belief that interesting data of that sort might be found by an application of the electrolytic or "forming" process. Although this feature was not a part of the program originally outlined, it was hoped that something bearing on the general question might be developed.

Electrolysis of ether solutions shows some features not common to aqueous solution. Ollar¹⁶ showed that in certain cases hydrogen was evolved at both electrodes, but he offered no explanation. Only a few papers¹⁷ have yet been published upon the electrolysis of Grignard reagents but work along that line is now being done. It is not possible to say just what happened in the cells treated in this paper, except that in some cases magnesium in the "tree" form was deposited on the cathode. Most of the deposit fell off the plate as soon as the current ceased, but the plate area may have been increased enough to account for at least a part of the increase in capacitance always noted. Luminescence has been observed during electrolysis, sometimes on the anode, sometimes on the cathode, sometimes on both plates.

In the electrolysis, a current of a few milliamperes at 15 volts was passed for 15 minutes through the phenylmagnesium bromide cells in the same direction as the current they generated. With the lower-resistance ethylmagnesium bromide cells 5 volts was applied for 5 minutes. With the first-mentioned type, the process resulted uniformly in decreased resistance, increased capacitance, and a light-resistance sensitivity where none had existed before. In the presence of light a decrease in resistance took place, while in a period of darkness equal to that of the illumination the original resistance was recovered. The ethylmagnesium bromide cells all developed capacitances 2 to 6 times the former values, but the resistance varied differently in different cells. No special change in light-resistance sensitivity was observed, except a small diminution in the magnitude.

Figs. 6 and 7 show results of tests with one cell of each type. Again no general relation was found between e.m.f., resistance, and capacitance changes under illumination. No resistance or capacitance effects were noted under x-ray irradiation.

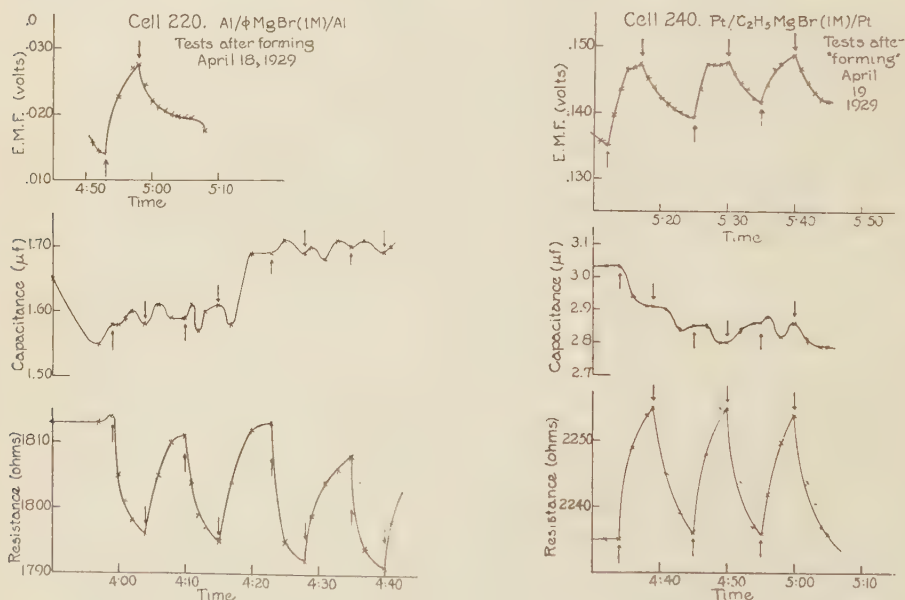
In several cases, cells measured with an ordinary d.c. Wheatstone bridge showed asymmetrical resistances somewhat like those shown by aluminum rectifiers, but the asymmetry was not so pronounced. In one case, the resistances to currents in opposite directions were 8000 and 16000 ohms respectively, while in another the figures were 2600 and 19000 ohms, the higher resistance being uniformly offered to a current opposite to the "forming"

¹⁶ A. Ollar, Thesis, University of Missouri (1926).

¹⁷ L. W. Gaddum and H. E. French, *Jour. Am. Chem. Soc.* **49**, 1295 (1927).

current. The aluminum rectifier stops a current flowing in the same direction as the forming current. The cells which showed this characteristic had aluminum plates and contained phenylmagnesium bromide. Such differences of resistance are not great enough to be of practical use.

One other interesting point remains to be discussed, but lack of exact knowledge of the chemistry of these cells forces rather vague conclusions. Films on aluminum in electrolytic condensers have been found to have thicknesses ranging from 10^{-2} to 5×10^{-6} cm and the dielectric constant was estimated as 14.5.¹⁸ Assuming a value of 1 for the dielectric constant in the present cases, film thicknesses have been computed for two cells which showed very large capacitances. An ethylmagnesium bromide cell gave over 7 mf per cm^2 after "forming". For $k = 1$, the film thickness was 1.2×10^{-3}



Figs. 6 and 7. Effect of light on e.m.f., resistance and capacitance.

cm. A phenylmagnesium bromide cell with copper plates showed about the same capacitance per unit area and the thickness figures were 8×10^{-8} cm. These figures are of the order of interplane distances in crystals, so it is possible that the films are single layers of molecules or a few such layers. It may be noted that the thickness attributed to the film in phenylmagnesium bromide, a benzene-ring compound, is greater than that found for ethylmagnesium bromide, a short-chain compound, as might be expected. The very large capacitance per unit area, 7 mf per cm^2 , is worthy of note. If these thickness figures are near the truth, it seems strange that regular light-capacitance effects were not found, especially in view of the fact that other evidence seems to indicate that the photovoltaic effect is dependent upon condition of the electrode surface.

¹⁸ H. O. Siegmund, Trans. Am. Elect. Chem. Soc. **53**, 203 (1928).

The following conclusions may be drawn.

(a) The conclusions of others as to variations in the e.m.f. of Grignard cells with age, with mechanical agitation, and with illumination are corroborated. The evidence seems to locate the seat of the phenomena at or near the surfaces of the electrodes.

(b) Several types of cells gave large voltage responses when exposed to x-rays and also showed large changes in current through a high-resistance circuit during such irradiation. The phenomenon is apparently a different one from the photovoltaic effect in the same cells.

(c) The resistance and polarization capacitance of a number of cells have been measured by means of a high-frequency bridge. Cells containing phenylmagnesium bromide showed no light-resistance response when freshly made, some containing ethylmagnesium bromide and one containing bromoethylmagnesium bromide did. This has been shown not to be a temperature effect. Some cells showed an increase of 1 or 2 percent in resistance when illuminated and some a decrease of about the same percentage, but a given cell was consistent. These results made a general photoelectric theory untenable and also indicated that the rather large voltage variations were not of the same origin as the resistance changes. The small reversible changes in conductivity were laid to alterations in solvation of the ions rather than to changes in ionization percentage. Such capacitance changes as were found seemed unrelated to other phenomena.

(d) A "forming" or electrolytic process was carried out with several cells containing phenylmagnesium bromide and ethylmagnesium bromide. The former then showed a light-resistance sensitivity. After the process, larger capacitances were observed in all cases, but no regular light-capacitance response.

Asymmetrical resistances, smaller than those in aluminum rectifiers, were found in a few cells.

Capacitances as high as 7 mf per cm^2 were found. Assuming a value of unity for the dielectric constant of the films, the probable thickness of the films was estimated to be of the order of the diameter of a molecule or a small multiple of that diameter. The thickness was greater for a benzene-ring compound than for the short-chain compounds used.

No effects on resistance or capacitance due to x-ray irradiation were detected.

In general, the evidence supports the belief that the voltage variations with illumination must be attributed to phenomena near enough to the electrodes to be affected by changes on their surfaces. The capacitance effects were inconclusive as to whether light-induced effects occurred in the films.

The writer expresses his sincere gratitude to Mr. R. T. Dufford, at whose suggestion the investigation was attempted and whose assistance and advice have been invaluable in carrying out the work; also to Professor O. M. Stewart for suggestions as to the bridge circuit and for the provision of the necessary apparatus and materials.

VITA

Harry Emmons Hammond received his elementary education in the public schools of Charlotte and Ann Arbor, Michigan. In 1905 he received the degree of Bachelor of Arts from the University of Michigan. From 1908 to 1918 he was engaged in teaching physics in the high schools of Newcastle, Indiana and Kalamazoo, Michigan. Graduate work at the University of Michigan in 1907-1908, summer of 1910, and in 1918-1919 led to the award of the degree of Master of Science in 1919. In 1918-1919 he was instructor in physics in the University of Michigan, the following year in Southeast Missouri State Teachers College, and from 1920-1929 in the University of Missouri. After further graduate work at the University of Chicago in the summer of 1922 and at the University of Missouri between 1920 and 1929, he received the degree of Doctor of Philosophy from the University of Missouri in 1929.

The work leading to the degree was carried out under the direction of Professors O. M. Stewart and H. M. Reese and with special assistance and advice of Mr. R. T. Dufford.

